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THIS ISSUE

Solvent Refining
and Dewaxing of
Lubricating Oil



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SOLVENT PROCESSING OF LUBRICATING OILS

PROCESSES employing selective solvents for the refining and dewaxing of lubricating oils have become a well established and important phase of the petroleum refining industry. These processes, on which Texaco research and development work has been outstanding, represent tremendous advances over earlier lubricating oil refining methods in that they permit the production of higher quality oils from a wider variety of starting materials at a lower cost.

In the solvent refining of lubricating oils, fractions carefully prepared by distillation procedures from selected crude oils, are intimately contacted with a selective solvent. The solvent and operating conditions employed are such that the undesirable constituents of the petroleum fraction are removed from the oil and may be withdrawn from the system as a separate stream. The refined oil is then subjected to dewaxing and other finishing processes. The solvent used is continuously recovered by distillation from the products leaving the extraction system and is returned to the latter for re-use.

In solvent dewaxing, a mixture of the dewaxing solvent and lubricating oil is cooled to a suitably low temperature as required for the crystallization of the wax as solid phase. These crystals are then removed by filtration and the dewaxed oil is recovered by distilling off the solvent which is returned to the system for further use.

For the refining step solvents such as sulphur dioxide, furfural, phenol, nitrobenzene and Chlorex (B, B¹ dichloro diethyl ether) may be used. Propane and various ketones, such as methyl ethyl ketone, mixed with aromatic hydrocarbons, such as benzene and toluene, have been employed. Furfural refining and ketone-aromatic solvent dewaxing have been extensively developed by Texaco scientists and engineers and are now widely employed in the industry under licenses from Texaco Development Corporation.

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Solvent Refining and Dewaxing of Lubricating Oil

THE CRUDE OIL as obtained from the well contains lubricating oil which has to be separated and purified prior to its use. Crude oil distillation is the first step and results in a segregation of the raw lubricating oil fractions. These raw fractions may be solvent refined to free them of low quality components which are potential sludge and carbon formers and which also have poor viscosity-temperature characteristics. If the solvent refined fraction still contains wax it may be removed in the solvent dewaxing process to provide a wax free oil which will remain fluid at low operating temperatures.

PREPARATION OF RAW LUBRICATING FRACTIONS

The selected crude oil as received at the refinery is subjected to a fractional distillation operation wherein the crude oil is split into the various desired portions according to the boiling temperature of the portion. The lowest boiling portion, and the first to be distilled, is the gasoline fraction while the other products in their respective order of removal are kerosine, diesel fuel, gas oil and the lubricating oil fractions. The light fractions such as the gasoline and kerosine are removed in an atmospheric distillation stage but the lubricating oil fractions are obtained by distillation under vacuum which permits vaporization to take place at temperatures sufficiently low that decomposition by cracking does not occur.

The distillation operation requires accurate and skillful control to assure that the proper grade of raw lubricating oil fractions are obtained. The operation of the vacuum still is maintained to provide fractions conforming to a limited range of variation for such tests as gravity, flash, fire, viscosity and others in order that after solvent refining and solvent dewaxing, the finished oils will conform to rigid specification values for the above-named tests as well as such other quality tests as viscosity index, pour test, carbon residue, neutralization number, demulsibility and numerous others which are criteria for the service of the lubricant in its intended final application and usage.

The lubricating oil fractions as obtained from the crude oil distillation unit are not suitable as quality lubricants and they contain poor quality components which vary widely in viscosity with changes in temperature as well as causing sludge and carbon formation when used at fairly high operating temperatures. The fractions also may contain wax which causes solidification to occur at temperatures as high as 100°F. It is therefore obvious that these undesirable components of the raw lubricating oil fractions must be removed in order to produce a finished oil which will function as a lubricant in an entirely satisfactory manner.

SOLVENT REFINING

Several processes employing various solvents

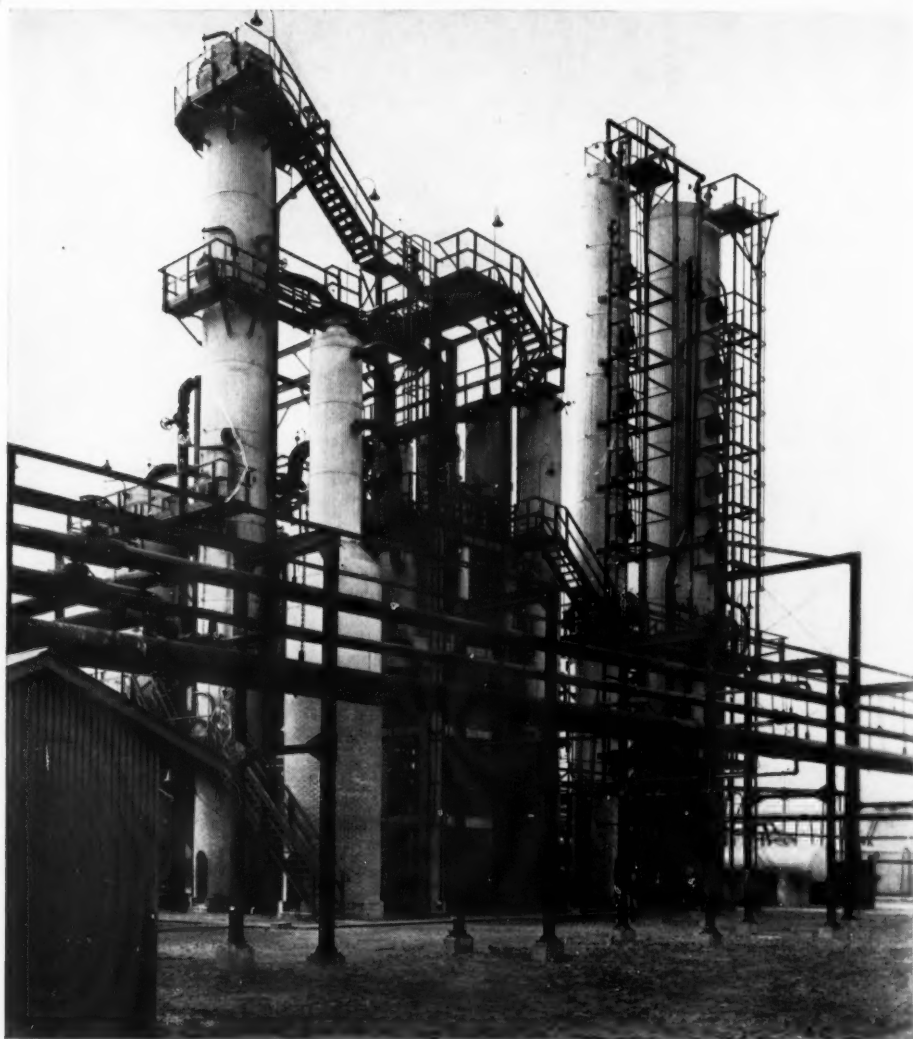


Figure 1—General view of a Furfural Refining Unit, showing treating tower, solvent recovery towers and solvent dehydrating system.

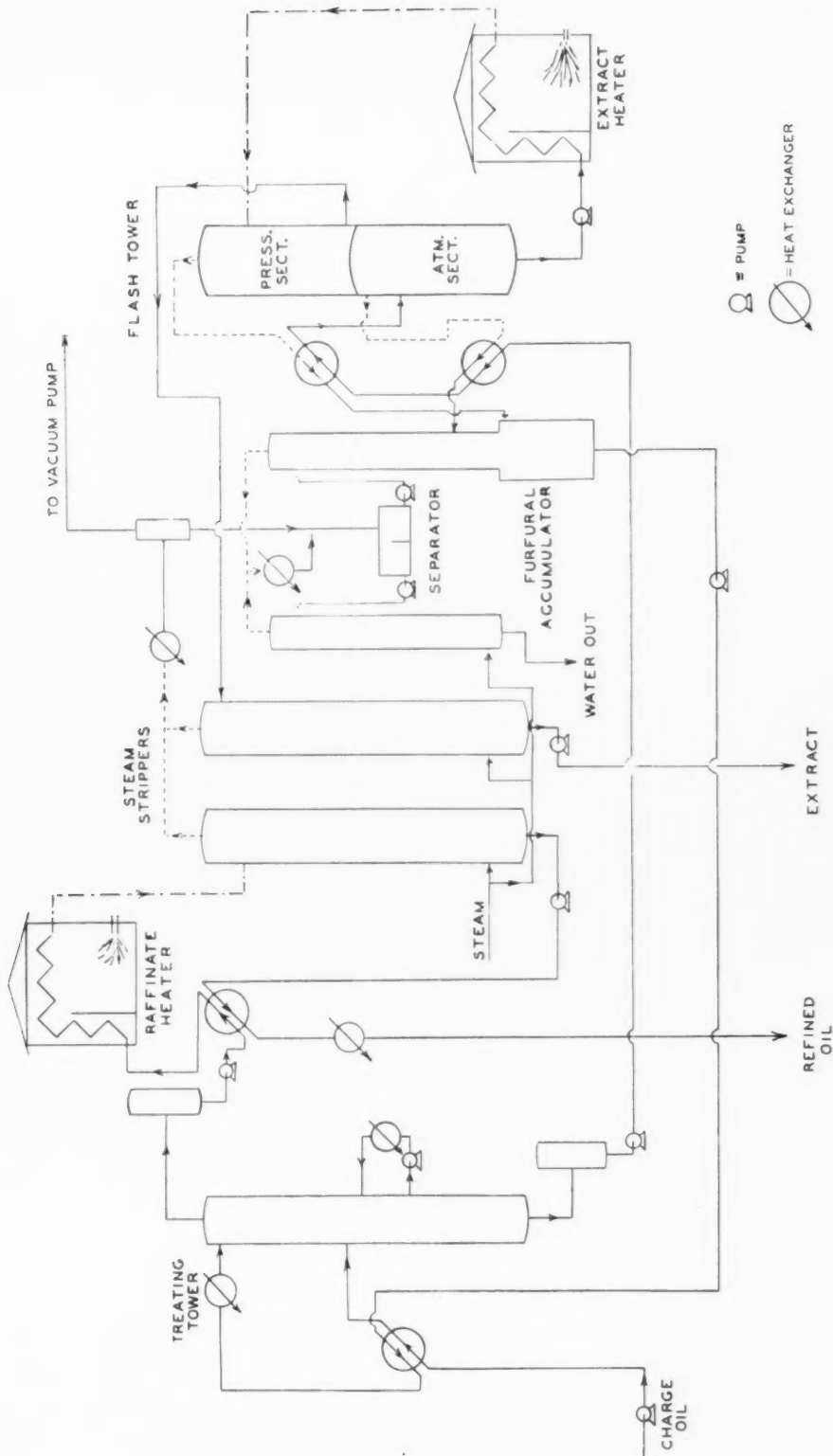
have been used for the purification by solvent refining of the raw lubricating oil fractions from the crude distillation unit. One of the most widely used of these processes is the Furfural Refining Process. In this process, furfural is used as the selective solvent to remove the undesirable components contained in the raw lubricating oil fraction.

Furfural is a chemical compound which is obtained commercially by digesting agricultural wastes such as oat hulls, straw, corn cobs, rice hulls, etc., with dilute sulfuric acid. The crude product from this digesting operation is purified by means of distillation. The purified product is essentially 100 per cent furfural which has the following physical properties:

| | |
|---|--------|
| Boiling point | 323°F. |
| Freezing point | -34°F. |
| Specific gravity at 68°F. | 1.1622 |
| Viscosity at 100°F., Saybolt Univ. sec. | 28.7 |
| Specific heat (68-212°F.) | 0.416 |
| Heat of vaporization, B.T.U. per lb. | 193.5 |
| Vapor pressure at 100°F., m.m. Hg. | 10 |
| Flash point (Tag. closed cup) | 138°F. |
| Solubility in water | 5.8% |

OPERATION OF FURFURAL REFINING PROCESS

Furfural possesses the property of selective solvent action which results in solution of the undesirable constituents of the raw lubricating oil fraction



SIMPLIFIED FLOW DIAGRAM FOR FURFURAL REFINING PROCESS

Figure 2

in the furfural solvent while the high quality oil components remain undissolved. There are two liquid phases formed when the raw lubricating oil and furfural are mixed and because of the high specific gravity of furfural as compared with oil, a separation of the phases is readily effected.

The lighter phase is called the raffinate solution and consists of approximately 90 per cent refined oil and 10 per cent furfural while the heavier phase consists of approximately 90 per cent furfural and 10 per cent undesirable oil components. This heavier phase is known as the extract solution. The temperature of the refining operation is controlled to remove the low quality components of the raw lubricating oil and the yield of refined oil varies with crude source. Some raw lubricating oil fractions contain a greater percentage of low quality constituents than others and higher extraction temperatures are necessary to remove the larger quantities of such undesirable components.

The solvent refining operation is illustrated in the Flow Diagram shown as Fig. 2. In commercial practice, the solvent refining or extraction operation is usually carried out in a packed tower. Raschig ring packing is used to provide a large amount of surface in order to attain the desired extraction of the low quality components from the raw lubricating oil fraction by the furfural.

Heated furfural from the solvent recovery unit is pumped to the top of the extraction tower and the raw lubricating oil fraction, heated to a temperature above the pour test, is pumped into the extraction tower at an intermediate point. The furfural flows downward in the tower and the oil flows upward. Commingling of the solvent and oil takes place due to the presence of the Raschig ring packing material.

The top of the tower is maintained at a higher temperature than the bottom so that as the oil flows

upward it is subjected to increasingly more severe extraction conditions. The refined oil or raffinate solution flows from the top of the tower and the extract solution flows from the bottom of the tower. These streams are charged to separate stripping towers where the furfural is removed by distillation and is returned to the extraction tower.

The solvent refining operation results in a purification of the oil product which is termed the raffinate. The impurities are contained in the extracted portion. This latter portion comprises those oil components which are readily oxidizable under conditions of final use of the finished lubricating oil. The relative tendency towards carbonization at high temperatures is measured by the Carbon Residue test value. Table I, below illustrates the reduction in carbon residue resulting from the furfural refining of various crude oil fractions. The solvent refined oil therefore is freed of the readily oxidizable and sludge forming components with the result that the refined oil may be used under severe operating conditions and will provide superior lubrication with a higher degree of cleanliness in the lubrication system. The solvent refining process also provides a product oil which is more susceptible to further improvement by the addition of oxidation inhibitors and other additives which permit satisfactory lubrication under extremely severe or special operating conditions.

The extract portion of the raw lubricating oil fraction also has a low viscosity index. The viscosity index* is an inverse expression of the relative rate of change in viscosity with change in temperature. Thus the extracted material becomes extremely viscous when it is cooled to temperatures of the order common in the winter season. The extract also contains those compounds removed from the raw lubricating oil fraction which would oxidize and carbonize readily at temperatures in the order of

*Reference—"Viscosity Index"—April, 1945—LUBRICATION.

TABLE I
FURFURAL REFINING OF FRACTIONS FROM MID-CONTINENT CRUDE

| | Medium Distillate | | | Heavy Distillate | | | Deasphalted Short Residuum | | |
|-------------------|-------------------|-------------------|---------|------------------|-------------------|---------|----------------------------|-------------------|---------|
| | Dewaxed Charge | Dewaxed Raffinate | Extract | Dewaxed Charge | Dewaxed Raffinate | Extract | Dewaxed Charge | Dewaxed Raffinate | Extract |
| Gravity, °API | 22.6 | 29.5 | 11.1 | 20.9 | 28.9 | 12.0 | 19.7 | 26.3 | 14.2 |
| Saybolt Universal | | | | | | | | | |
| Viscosity | | | | | | | | | |
| at 100°F. | 480.5 | 249.3 | | 1614 | 567.9 | | 9358 | 2929 | |
| at 210°F. | 55.3 | 49.3 | 88.1 | 89.7 | 64.5 | 186.7 | 254 | 161.8 | 387 |
| Viscosity Index | 52.3 | 96.9 | | 43.5 | 96.3 | | 63.4 | 92.8 | |
| NPA Color | 8 | 3½ | | 8+ | 3+ | | | | |
| Carbon Residue | 0.28 | 0.02 | | 1.05 | 0.02 | | 2.4 | 0.44 | |

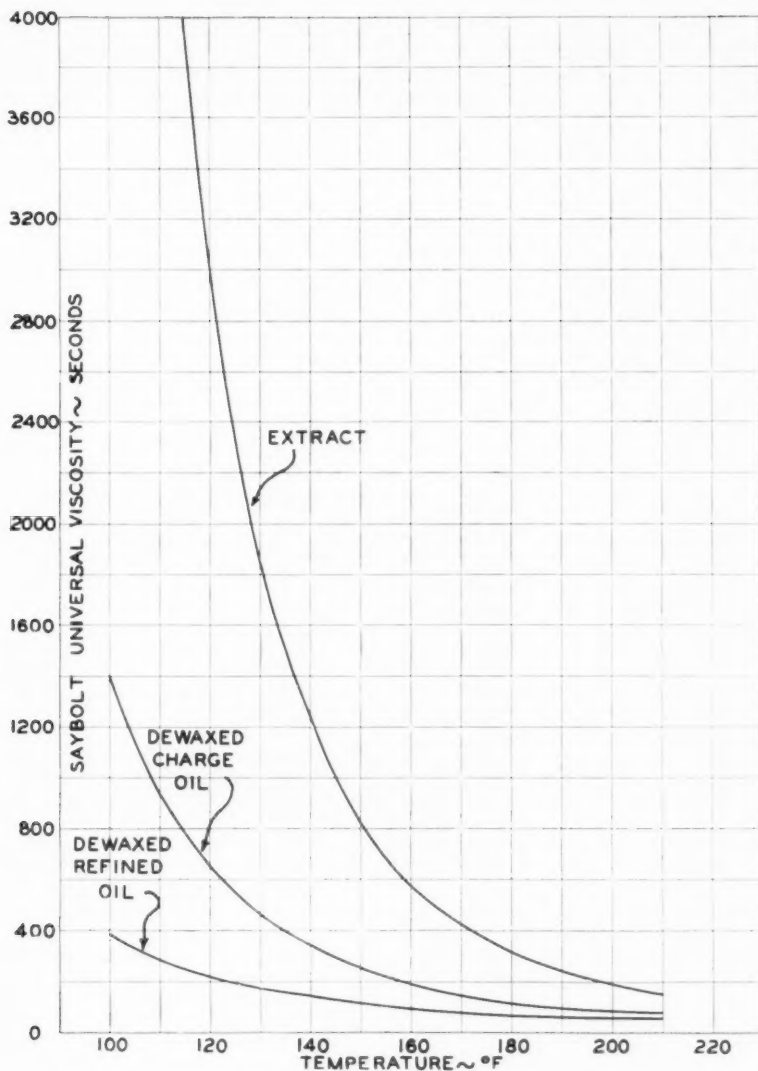


Figure 3—The solvent refined oil is improved over the charge oil in regard to the rate of change in viscosity with change in temperature.

those existent for instance in an internal combustion engine.

The effect of furfural refining upon the viscosity-temperature relationship is illustrated graphically by Figure 3. It will be seen that furfural refining has resulted in a refined oil whose viscosity does not vary greatly as the temperature changes. This is of importance since the oil does not become as thin or non-viscous at high operating temperatures and also does not thicken or become as excessively viscous at low operating temperatures. As an illustration of this, a motor oil that has been properly solvent refined will permit easy starting of the automotive engine at low winter temperatures and will also continue to provide proper lubri-

cation after the engine has attained the operating temperature.

SOLVENT DEWAXING

In many instances where paraffinic type crudes are involved, the resulting solvent refined oils contain sufficient wax to make them unsuitable for use over the range of temperature encountered in the intended service. When the wax contained in the undewaxed refined oil crystallizes upon cooling the oil, the crystals form a network or matrix which holds the oil and the mass becomes solid or semi-solid. Under this condition the oil will not flow or be moved by gravitational forces. Although it may be forced to flow by application of very high pressure, the waxy oil will not spread over a metal surface to be lubricated. Furthermore, the semi-solid character of the waxy oil at winter temperature would necessitate the development of an extremely high torque for the starting of an automotive engine for instance. Aside from the fact that the wax solidifies in oil at temperatures below 100°F., it also has the disadvantage of having a low viscosity at the high operating tempera-

tures and does not provide good lubrication. For these reasons wax must be removed to provide a finished lubricating oil of good quality which will flow freely at low temperatures.

Of the various processes which have been employed for this purpose such as cold settling, cold pressing (filtration without diluent), centrifuging of naphtha diluted and chilled oil, and filtration after dilution with a selective solvent and chilling, the latter has been found most satisfactory and is now enjoying widespread use in the petroleum industry.

The solvent most generally used in the Solvent Dewaxing Process is a mixture of methyl ethyl ketone and benzol. The ratio of the ketone to

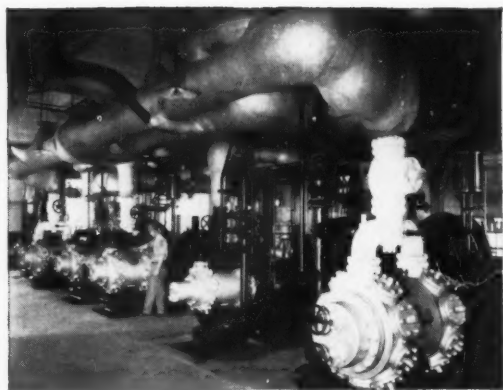


Figure 4—View of ammonia compressors in a refrigeration plant for a solvent dewaxing unit.

benzol is adjusted to prevent any separation of liquid oil when the solution is chilled to the filtering temperature. With the use of the proper solvent and when suitable chilling rates are employed, the wax is separated in crystals with a minimum occlusion of oil and in form which permits their being separated from the oil-solvent mixture by filtration at high rates of filter thruput.

The flow for solvent dewaxing is shown in Figure 7. In a typical operation, the waxy refined oil is mixed with the solvent in the correct proportion at a temperature of about 120°F., at which temperature the oil and wax are dissolved in the solvent. The solution passes through double-pipe heat exchangers where some refrigeration is recovered from the cold filtrate solution from the rotary vacuum filter. The solution is further chilled by direct expansion of ammonia in double-pipe chillers which are equipped with scrapers to prevent the accumulation of solid wax on the inner surface of the center pipes.

The chilled solution containing the solidified

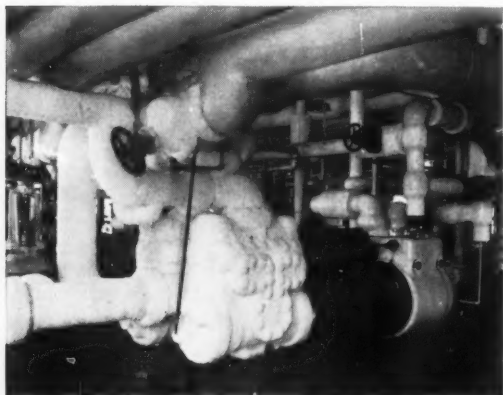


Figure 5—View of pump room in a solvent dewaxing plant. The pump in front is handling filtrate solution from the filters to exchangers.

wax flows from the double-pipe chiller to the rotary vacuum filter. The drum of the filter rotates and the level of the solvent-oil-wax mixture is such that about one-half of the drum is submerged. Filtration occurs on the portion of the drum which is submerged and as this portion approaches the top in its rotation, a wash is applied on the wax cake by spraying with chilled solvent. In the further rotation, the cake is dried by the inert gas (contains substantially no oxygen) pulled through the wax cake by the vacuum existing inside the drum. Following this, a slight positive gas pressure is applied as the wax cake approaches the scraper blade which causes the wax to fall into a screw conveyor which discharges the slack wax from the filter to the slack wax surge tank. From this tank the wax is pumped to the wax flash tower where

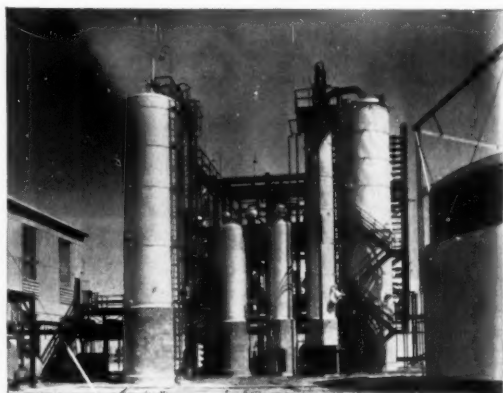
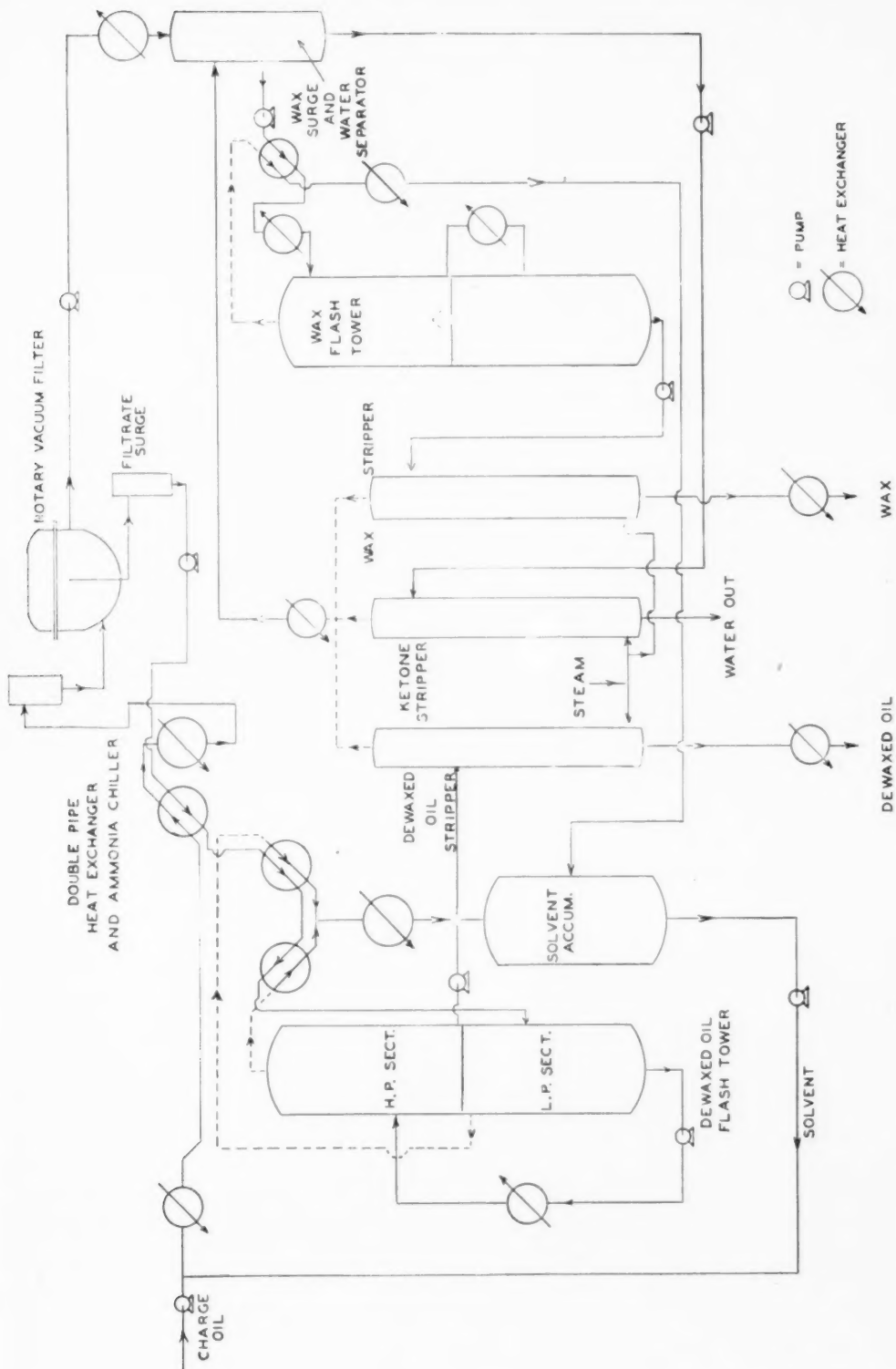


Figure 6—Solvent recovery towers for solvent dewaxing plant. The filter building is shown at the extreme left and inert gas holder is on the right.

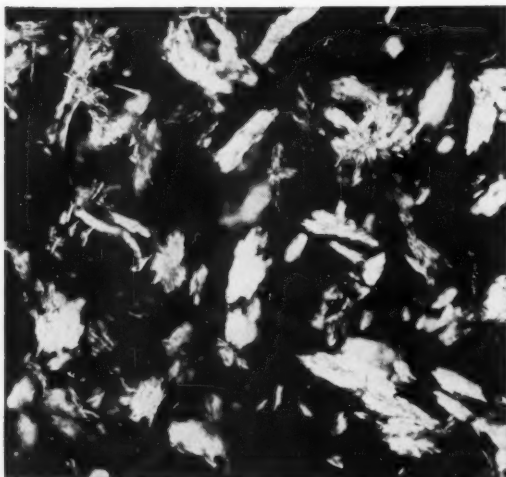
the major part of the solvent is removed by distillation. Removal of the final traces of solvent is accomplished by steam stripping in the wax stripper tower. The stripped wax is cooled and pumped to storage.

The dewaxed filtrate flows from the vacuum filter into the filtrate surge tank from which it is pumped through the double-pipe heat exchangers, where refrigeration is recovered, and then through low pressure and high pressure vapor heat exchangers. Sufficient heat is absorbed by the filtrate solution in the exchange equipment to cause a considerable quantity of the solvent to be vaporized in the low pressure section of the dewaxed oil flash tower. The bottoms from the low pressure section of the flash tower are pumped through a heater to the high pressure section. The heat from the vapors of this section is used, by means of the exchange equipment, to cause vaporization of solvent in the low pressure section. The bottoms from the high pressure section are freed of the final traces of

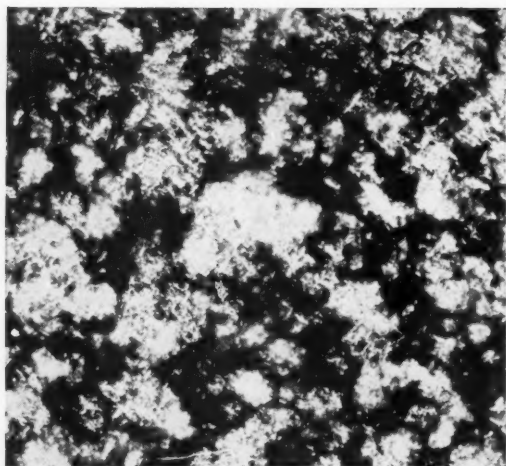


SIMPLIFIED FLOW DIAGRAM FOR SOLVENT DEWAXING PROCESS

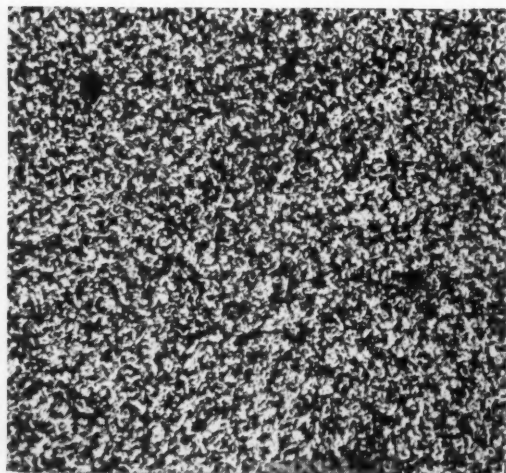
Figure 7



A



B



C

solvent by open steam stripping in the dewaxed oil stripper. The steam stripped dewaxed oil is then pumped through a cooler to oil storage.

The wax contained in the refined oil varies widely with the character and viscosity grade of the oil fraction as illustrated by the photomicrographs of Figure 8. The light or low viscosity distillate fractions contain wax which crystallizes in large plate or needle shapes and with increasing viscosity grades the wax crystals become smaller. The refined residual stocks contain microcrystalline wax, the crystals of which are very small. The solvent dewaxing process is sufficiently flexible to allow good operation despite the variation in the size and character of the wax crystals.

The wax removed from the light distillate refined oil is markedly crystalline in character and, when a slab is subjected to bending to the breaking point, shows crystalline appearance on the broken edges. The wax or petrolatum removed from the refined residual stock when distorted by bending shows a certain degree of plasticity and will therefore bend to a considerable extent before breaking.

SUMMARY

1. The solvent refining process produces a refined oil which has been freed of components susceptible to oxidation, sludge formation and carbon deposition.
2. The solvent refined oil is very amenable to further improvement by the use of oxidation inhibitors and other additives.
3. Solvent refining improves viscosity index and therefore the oil does not become as extremely viscous at low temperatures and also does not become as thin at the higher operating temperatures.
4. The wax contained in lubricating oil fractions must be removed to provide a finished oil which will flow readily at low temperatures.
5. The solvent dewaxing process provides a dewaxed oil which will remain fluid at the low temperatures.
6. The solvent dewaxing process is flexible in operation and is applicable to a wide variety of lubricating oil stocks.

Figure 8—Photomicrographs of wax crystals show that the sizes of crystals vary greatly for various lubricating oil fractions.

A—Photomicrograph of wax crystals from light lubricating distillate in methyl ethyl ketone-benzol solution. Magnification 75X.

B—Photomicrograph of wax crystals from heavy lubricating oil distillate in methyl ethyl.

C—Ketone-benzol solution. Magnification 75X. Photomicrograph of wax crystals from residual lubricating oil in methyl ethyl ketone-benzol solution. Magnification 75X.

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